An Early Attempt to Oxidise Gold

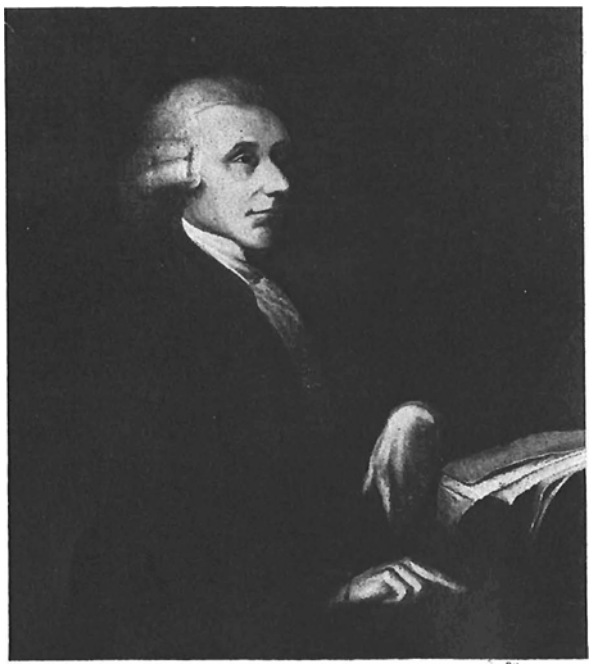
VAN MARUM'S LARGE ELECTROSTATIC GENERATOR AND THE SWAN SONG OF PHLOGISTON

W. D. Hackmann
Museum of the History of Science, Oxford

The complete immunity of gold to oxidation was not always understood in the early days of chemistry. The Dutch chemist Van Marum, reluctant to abandon the concept of phlogiston, carried out a remarkable series of experiments on the oxidation of metals—including an unsuccessful attempt to oxidise gold—that was crucial to the general acceptance of Lavoisier's new theory of combustion and reduction and thus to the final abandonment of the erroneous phlogiston theory.

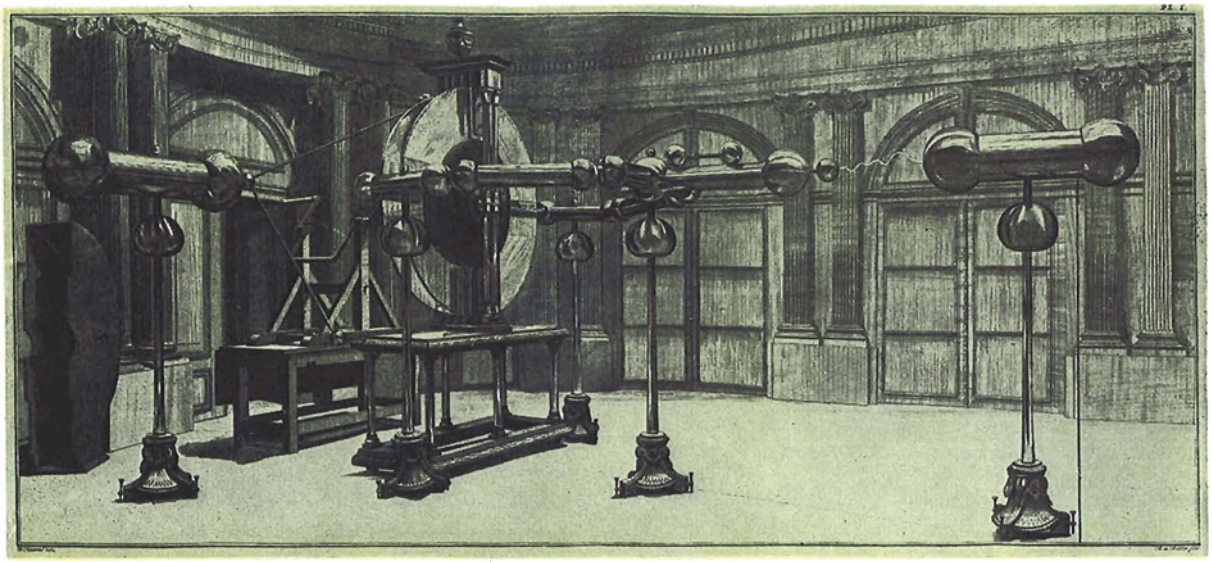
During the winter of 1786 the Dutch scientist Martinus Van Marum conducted a series of remarkable experiments on the oxidation and reduction of metals by subjecting them to electric discharges produced by a vast triboelectric generator. Among the metals was gold, and although Van Marum believed, from the purple colour of the powder produced, that he had succeeded in preparing the calx or oxide, this experiment had, of course, resulted only in the dispersion of the gold into a very finely divided form. The whole series of experiments was, however, vital to the acceptance of Lavoisier's new theory of oxidation that had been explained to him during his visit to Paris in July 1785.

The "extraordinarily large" triboelectric generator, or frictional electrical machine, was constructed for the Teyler Foundation in Haarlem on Van Marum's advice in 1784 (1). He had been appointed Director of the "Cabinet of Physical and Natural Curiosities" of this Foundation, and thought that, if there were constructed a generator superior to any that had hitherto been used, new discoveries would undoubtedly be made. Teyler's generator was greatly admired throughout Europe and scientists flocked to Haarlem to see it. It was built by the English instrument maker John Cuthbertson, who lived in Amsterdam from about 1768 to 1797 and who was largely responsible for the development of the



Joseph Priestley
1733–1804

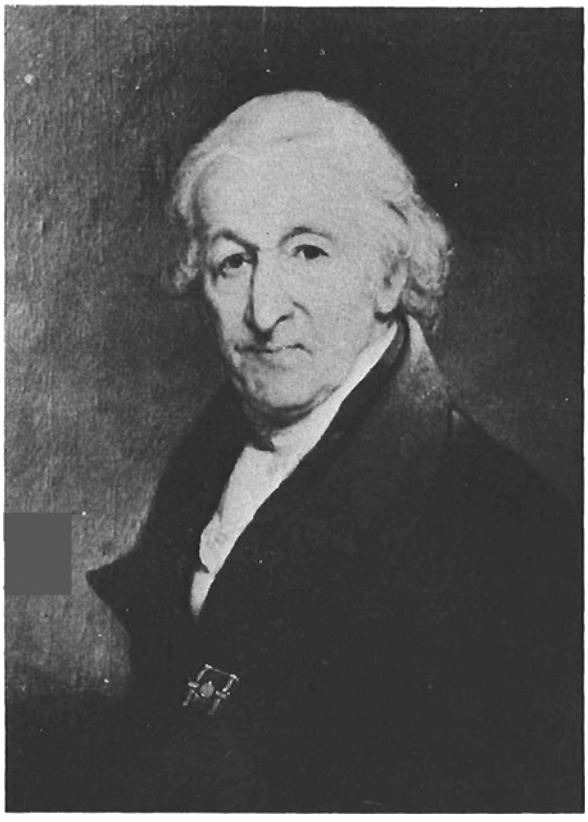
Two hundred years ago—on August 1st, 1774—Priestley first prepared oxygen at the home of his patron Lord Shelbourne at Calne in Wiltshire by focusing his large new burning glass upon red oxide of mercury. He called the gas "dephlogisticated air", and despite his discussions in Paris later in the same year with Lavoisier, then developing his theory of combustion, Priestley never accepted the newer ideas of oxidation and reduction and remained a confirmed phlogistonist all his life. His own experimental attempts to oxidise gold he regarded as inconclusive



This extraordinarily large electrostatic generator was built in 1784 by the English instrument maker John Cuthbertson for the Dutch scientist Van Marum. Its two glass plates were 65 inches in diameter, and had to be turned by two men standing on a specially constructed table. It could strike a spark two feet in length between its brass electrodes, and was used by Van Marum to study the oxidation and reduction of metals by subjecting them to its discharge. His results convinced him of the errors of the phlogiston theory and of the rightness of Lavoisier's newly advanced ideas on oxidation and reduction.

electrostatic plate machine and for its popularity in the Netherlands. Teyler's electrical machine consisted of two glass plates 65 inches in diameter which had to be turned by two men standing on a specially constructed table. Its brass prime conductor, on which the charge was collected, was more than five feet long and the longest discharge that could be produced was two feet; in modern terms this represents about 500,000 volts. For his electrochemical experiments performed in 1786 Van Marum also employed a battery of Leyden jars containing 225 square feet of coated glass.

In 1766 Priestley noticed a "black stain" when he passed a discharge through a brass chain lying on a sheet of white paper. At first he thought that this was dust shaken off the chain by the discharge, but after repeating the experiment with a number of metals he concluded that the deposit produced by each discharge must be the calx of the metal, or the calx



Martinus Van Marum

1750 – 1837

Born in Delft, Van Marum graduated at Groningen University in medicine and botany in 1773 and then moved to Haarlem, where he was appointed Director of the "Cabinet of Natural Curiosities" of the Hollandsche Maatschappij der Wetenschappen. In 1784 he became librarian of the Teyler Stichting in Haarlem and the Director of its museum. Like other chemists of this period, Van Marum did not realise that gold could not be oxidised but thought that if he was successful in oxidising this metal, as he expected to be with his very powerful discharges from the electrostatic generator, it would support Lavoisier's views on oxidation

of the metal and phlogiston. The name "phlogiston" had been given by the German chemist Georg Ernst Stahl of Halle in 1697 to a substance that was thought to leave a burning body. A "calx" was a metal which had lost its phlogiston on heating, a process which was known as "calcination". During "revivification", phlogiston was thought to unite with the calx and to revive it to its metallic state.

Priestley's Calcination Experiments

In his calcination experiments Priestley produced the same black powder with gold and silver. He could not at first believe that he had produced a calx, as chemists generally thought that it was impossible to calcine these metals, so he repeated the experiment with the purest gold he could obtain. When he passed a discharge through a few grains of gold placed on a piece of paper most of them were dispersed all over the room by the explosion and he noticed a black stain on the paper "intermixed with red making an odd motley appearance". Next, he placed a small piece of gold leaf in a quill and passed a discharge through it. The quill was tinged with a beautiful vermilion red, but this time there was no black powder, and Priestley decided that his experiments on the calcination of gold were inconclusive. The physicist John Canton, however, had made similar experiments, and produced the same colours, and, according to Priestley, these clearly proved the calcination of pure gold and silver by the heat of the "electrical explosion".

Despite Priestley's own success in preparing oxygen—which he called "dephlogisticated air"—in 1774 and his discussions later in the same year with Lavoisier, who was then developing his theory of combustion, he never accepted the newer ideas of oxidation and reduction and remained a confirmed phlogistonist all his life.

When Van Marum started his own experiments with metals in 1784 it was generally accepted that all metals could be calcinated by the electric discharge. A controversy had, however, developed about the discovery by the Italian scientist Beccaria that strong electric discharges could also revive (reduce) the metal calces (2). In 1775 a series of experiments made by the Frenchmen Brisson and Cadet seemed to support their idea that this revival was the result of the fusion of the conductors between which the calces had been placed (3). Van Marum decided in favour of Beccaria's theory, and, assisted by Cuthbertson and the Dutch chemist Paets Van Troostwijk, managed to reduce the oxides of several metals in a dramatic series of experiments. In these experiments the glass plates between which the metal strips were pressed were shattered by the discharges and coated with the reduced metals (4). Van Marum concluded that the calces could only have received phlogiston from the electric matter, and that this was the cause of the revivification. He next demonstrated that electric discharges could indeed also produce metal calces. This result rather worried him, because it now seemed that electric matter was capable of both donating and abstracting phlogiston. He was unable to explain these results:

> "When comparing calcination here with the revivification in the preceding Chapter it seems on the surface rather contradictory; for the same cause seems to produce opposite phenomena. However, fire can also produce these two opposite effects on metals and on the calces . . . I can at present not give any further explanation."

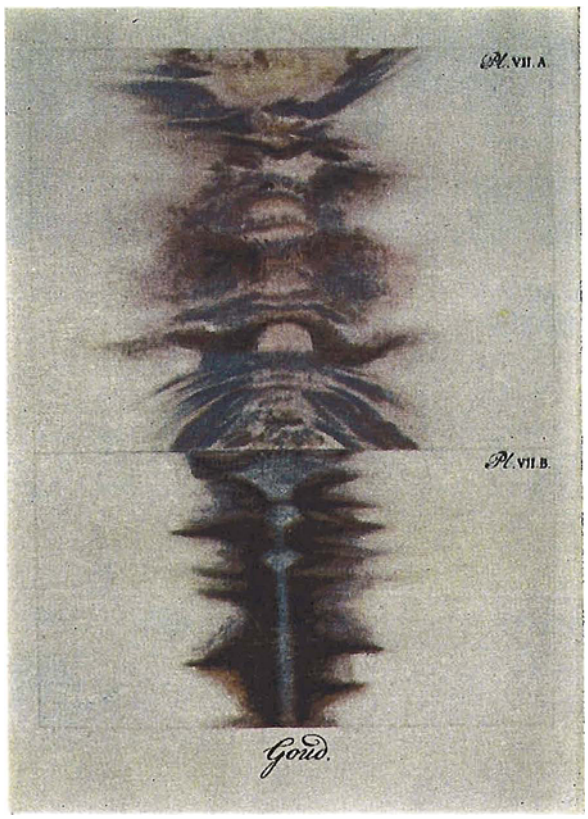
Van Marum's visit to Paris in July 1785 shattered his faith in the phlogistic framework of his theories on combustion and on the nature of electricity. He met many scientists, including Benjamin Franklin and Lavoisier. He gave the former his "proof" of the existence of a single electric fluid, and discussed with Lavoisier the contradictory results of his calcination and revivification experiments. Lavoisier's new theory of combustion was explained to him in great detail, especially by Berthollet and Monge, two of Lavoisier's few staunch supporters. They offered confirmation in the form of elegant experiments, including the synthesis of water from its elements by continuous combustion and gravimetric experiments on calcination and combustion. On his return to Haarlem, Van Marum at once repeated and extended his calcination and revivification experiments. Like those Priestley had made twenty years before, they included a series of experiments in which gold and other metals lying on pieces of white paper were subjected to electric discharges to enable the configurations so produced to be studied.

As with other chemists of the time Van Marum did not realise that gold was extremely inactive, but thought that it was difficult to oxidise. Thus if he was successful in oxidising gold, as he fully expected to be able to do with his very powerful electric machine, it would be a further proof of the rightness of Lavoisier's theory.

Van Marum's Purple Deposits

Van Marum described in detail what happened when he subjected gold wires of different lengths and diameters to electric discharges (5). In all these experiments, he saw a thick smoke rise up and a purple deposit on paper. Sometimes, he also produced globules of molten gold, and in one instance he collected these in a four-inch-wide paper cylinder. Where the globules had hit the paper, marks were left by the purple powder with which the globules were coated. His experiments also seemed to indicate that gold wire which was just allowed to glow by

Van Marum was so impressed by the colours and configurations produced by passing the discharge through gold wires that he had them painted by J. C. Sepp of Amsterdam, an artist well known for his natural history illustrations. This plate shows the colours that he supposed to be produced by calcination of gold, although they are, of course, merely due to the pulverisation of the gold by the discharge



means of an electric discharge continued to calcinate on its surface for as long as it remained glowing. He considered the colours and configurations produced so beautiful that he had them drawn by J. C. Sepp of Amsterdam, an artist well known for his fine illustrations for works on natural history. Van Marum included these plates in Volume 4 of the *Verhandelingen, uitgegeven door Teyler's Tweede Genootschap*, in which these calcination experiments were described. The plate on the supposed calcination of gold, reproduced here, is a particularly fine one. Van Marum assumed the colours to be caused by the calcination process, although they must, of course, be ascribed only to the pulverisation of the gold by the electric discharge.

Van Marum was not the only scientist to believe that the colours produced in these experiments were caused by the oxidation of metals. He assumed that the amount of the principle of pure air (oxygen) which united with the metal depended on the degree to which it had been heated by the discharge. Berthollet had demonstrated this in 1785 with the calcination of iron, when he concluded that the colour varied with the amount of pure air which had united with the metal.

The Spread of Lavoisier's Theory

Van Marum conducted many more experiments on the calcination of metals, including attempts to calcine wire under water, and also experiments on the composition of water. These convinced him of the truth of Lavoisier's new theory of combustion. Since Lavoisier's work was still practically unknown in Holland he included in the *Teyler's Verhandelingen* of 1787 an appendix entitled "An Outline of the Doctrine of M Lavoisier" (6). This was based on Lavoisier's "Opuscules Physiques et Chimiques" of 1774, and on his scientific publications published between then and 1785. It was the first coherent exposition of the "antiphlogistic system" in the Netherlands or any other country, including France, and had a great influence on the diffusion and acceptance of Lavoisier's ideas in the Netherlands.

In Van Marum's experiments the great power of the Teyler Foundation's large electrical machine played a decisive part, for it allowed him to conduct experiments on a scale that had hitherto been impossible. In the past, the amount of metal oxide that could be produced, or be reduced, was so small that it was difficult to draw conclusions. The huge discharges produced by Van Marum's large machine and the battery of Leyden jars clearly showed whether a change had taken place. This machine often allowed Van Marum to act as an arbitrator (if an uninvited one) between contending theories. It may have been luck, or perhaps astuteness, which made him usually support those theories which in time proved to be correct.

References

1 M. Van Marum, "Journaal mijne verrichtingen ter verkrijging eener verzameling van physische instrumenten", entries for 1783. Van Marum Archives, *Hollandsche Maatschappij der Wetenschappen*, Haarlem. MS 17 (b)
2 G. B. Beccaria, "Dell'electricismo", Turin, 1785, 282
3 M. J. Brisson and L. Cadet, *Mem. Acad. r. Sci. Paris*, 1775, 243
4 M. Van Marum, "Beschrijving eener ongemeen groote electrizeer-machine, geplaatst in Teyler's Museum te Haarlem, en van de proefneemingen met dezelve in 't werk gesteld", *Verh. Teyler's Gen.*, 1785, **3**, 183–191
5 M. Van Marum, "Eerste vervolg der proefneemingen, gedaan met Teyler's electrizeer-machine", *Verh. Teyler's Gen.*, 1787, **4**, 93–97
6 "Schets der Leere van M Lavoisier", *Verh. Teyler's Gen.*, 1787, **4**, 235–266